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(54) WHITE ALIPHATIC POLYESTER FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject film useful for wrapping applications which is excellent in printing clarity, manual cuttability and twist fixability by constituting the film from a polymer having an aliph. polyester as the main component, and by making the film have a specific light transmittance.

SOLUTION: This film is constituted from a polymer comprising, as the main component, an aliph. polyester having a main repeating unit represented by the formula: O-CHR-CO, pref. a polylactic acid. The film is made to have a light transmittance of ≤50%. In the formula, R is H or a 1-3 C alkyl. Preferably, the film is at least uniaxially stretched to be oriented. The stretching temp. is pref. in the range from the glass transition temp. of the polymer to the temperate +50°C. The film pref. comprises inactive particles which are inorg. particles and/or org. particles inside the film. As the particles, exemplified are TiO₂, CaCO₃, BaSO₄, ZnO, SiO₂, talc, kaolin, PS particles, zeolites, or the like. Furthermore, a coated layer is formed at least on one surface of the film, as necessary.

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CLAIMS

[Claim(s)]

[Claim 1]A white aliphatic polyester system film which consists of polymer which uses as the main ingredients aliphatic polyester whose main repeating unit is general formula-O-CHR-CO- (R is hydrogen or an alkyl group of the carbon numbers 1-3), and is characterized by light transmission being 50% or less.

[Claim 2]The white aliphatic polyester system film according to claim 1, wherein said aliphatic polyester is polylactic acid.

[Claim 3]The white aliphatic polyester system film according to claim 1 or 2, wherein said film is carrying out orientation to at least 1 axis.

[Claim 4]The white aliphatic polyester system film according to claim 1 to 3 containing an inorganic particle and/or organic particles inside said film.

[Claim 5]The white aliphatic polyester system film according to claim 1 to 4 providing a coating layer at least in one side of said film.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is a film which consists of aliphatic polyester system resin. If it says in more detail, in the films for a package and the objects for tapes, such as a perishable food, a processed food, drugs, medical equipment, and electronic parts, it excels in the printing clear nature, solatium nature, and twist nature which are the important characteristic, and is related with an aliphatic polyester system film useful as the object for a package, or an object for tapes.

[0002]

[Description of the Prior Art]Conventionally, aliphatic polyester films including polylactic acid have been developed considering it becoming a harmless decomposition product by a microorganism to decompose, when rejected under natural environment, for example, a polylactic acid film, after hydrolyzing automatically in soil as a feature. As such a film, it consists of a polylactic acid system polymer, and planar orientation degree deltaP is more than 3.0×10^{-3} , And the film which excelled [difference / (delta Hm-delta Hc) / of amount of crystallization heat of fusion deltaHm when temperature up of the film is carried out, and crystallization-heat-quantity deltaHc generated by crystallization in temperature up] in the intensity and thermal dimensional stability which are 20 or more J/g is indicated to JP,7-207041,A.

[0003]However, as a result of giving priority to making it decompose in a nature and furthering development, the outstanding characteristic which aliphatic polyester originally has was not fully able to be pulled out. That is, since hydrolysis and decomposition by a microorganism were controlled when the orientation and crystallization of a film progress, intensity and thermal dimensional stability were insufficient.

[0004]Cellophane is known as a film which was excellent in solatium nature from the former. Cellophane is appointed to a position of a trust as an object for various wrapping and adhesive tape with the characteristics, such as the outstanding transparency, easy-tearability, twist wrinkles stability. However, on the other hand, since it had hygroscopicity, cellophane was difficult to change the characteristic according to a season and to supply fixed quality. Although the extended polyethylene terephthalate film is excellent in the outstanding characteristics, such as toughness, heat resistance, a water resisting property, and transparency, When it was used as base materials, such as a bag for a package, and adhesive tape, it was

hard to cut, and since the fault which cannot tear the mouth of the bag for a package easily, the fault which adhesive tape cannot cut easily, and twist stability were inferior, there was a fault that it could not use for a twist package.

[0005]What (JP,56-50629,B) carried out copolymerization of the polyester film (JP,55-8551,B) which carried out orientation, the diethylene glycol component, etc. is used for 1 shaft orientations as a method of solving said solatium nature and twist stability.

[0006]However, although the method of carrying out uniaxial orientation in the above-mentioned conventional technology was linearly turned off easily to the orientation direction, it could not be easily turned off other than the orientation direction, and the method of carrying out copolymerization of the other ingredients had the fault that the original characteristic of polyethylene terephthalate was spoiled.

[0007]

[Problem(s) to be Solved by the Invention]This invention solves an above-mentioned problem and an object of this invention is to provide the aliphatic polyester system film which is excellent in printing clear nature and solatium nature useful as substrates the object for a package, for printing, etc., and twist stability.

[0008]

[Means for Solving the Problem]The white aliphatic polyester system film which this invention was made in view of the above situations, and was able to solve the above-mentioned technical problem is as follows.

[0009]1. White aliphatic polyester system film which consists of polymer which uses as the main ingredients aliphatic polyester whose main repeating unit is general formula-O-CHR-CO- (R is hydrogen or alkyl group of carbon numbers 1-3), and is characterized by light transmission being 50% or less.
2. White aliphatic polyester system film of said one statement, wherein said aliphatic series system polyester is polylactic acid.

3. White aliphatic polyester system film given in said 1 or 2, wherein said film is carrying out orientation to at least 1 axis.

4. White aliphatic polyester system film given in said 1 thru/or 3 containing inorganic particle and/or organic particles inside said film.

5. White aliphatic polyester system film given in said 1 thru/or 4 providing coating layer at least in one side of said film.

[0010]

[Embodiment of the Invention]The aliphatic polyester used by this invention makes general formula-O-CHR-CO- (R is hydrogen or an alkyl group of the carbon numbers 1-3) a main repeating unit. As such aliphatic polyester, although polylactic acid, polyglycolic acid, poly (2-oxybutanoic acid), etc. can be mentioned, for example, it is not limited to these. Depending on the case, independent [these] may be sufficient, or it does not matter even if it uses a mixture and a copolymer. Although optical isomers, such as L-object, DL-object, and D-object, exist, those any may be sufficient as the thing which has asymmetrical carbon in polymer, and the mixture of these isomers may be sufficient as it. The polymer used as the raw material of these films mentioned above is manufactured by publicly known methods, such as carrying out ring opening polymerization of the corresponding drying cyclic ester compound of alpha-oxy acid.

[0011]As for the reduced viscosity (etasp/C) of said aliphatic polyester system resin, in this invention, it is preferred that it is [or more 0.50] 2.50 or less. There are many fractures at the time of film production that

reduced viscosity is less than 0.50, the physical properties of the film obtained further are remarkably inferior, and catabolic rate is too quick and does not attain the purpose of this invention easily. The solutium nature of the film which will be obtained on the other hand if reduced viscosity is larger than 2.5, and twist nature not only fall, but since melt viscosity becomes high, it is easy to produce the problem that melt extruding becomes difficult. The range of still more desirable reduced viscosity is 1.80 or less [0.50 or more] more preferably 2.0 or less [0.50 or more].

[0012]The aliphatic polyester system film of this invention requires that light transmission should be 50% or less, and is 20% or less especially preferably 30% or less preferably. The method in particular for making light transmission of said film into 50% or less is not limited. For example, the method of painting the surface, the method of sticking paper, a nonwoven fabric, etc., the method of making inert particles, such as an inorganic particle and/or organic particles, contain inside a film, or the method of making many caves contain inside a film is mentioned. Especially, it is preferred to apply the method of making the cave of the method and/or a large number which make inert particles, such as an inorganic particle and/or organic particles, containing containing to the inside of a film.

[0013]Inert particles made to contain inside a film, such as an inorganic particle and/or organic particles, although not limited in particular, the difference of a refractive index with aliphatic polyester is big. A titanium dioxide, calcium carbonate, barium sulfate, a zinc oxide, a silicon dioxide, particles [inertness / flocs / magnesium carbonate, a strontium carbonate, an aluminum oxide, talc, kaolin, zeolite, benzoguanamine particles, polystyrene particles, / secondary / such] – one kind -- or two or more kinds can be used.

[0014]In order to make many caves contain inside a film, for example, aliphatic polyester is made to mix and distribute the thermoplastics of immiscible nature with an extruder, the cast is carried out to cooling drum lifting, an unextended sheet is obtained, and the method of subsequently to at least one or more axes extending is mentioned. By extending an unextended sheet on at least one or more axes, exfoliation takes place by the interface of aliphatic polyester and the thermoplastics of immiscible nature, and many caves occur in a film. If it is resin which forms a cave in the inside of a film at the time of extension as thermoplastics of said immiscible nature, it is not restricted at all but is arbitrary, but polyolefin system resin, poly acrylic resin, polycarbonate system resin, polysulfone system resin, cellulose type resin, etc. are mentioned. Also in it, polyolefin system resin, such as polystyrene, polypropylene, and a polymethylpentene, is especially preferred.

[0015]The inert particle of said statement of organic particles, an inorganic particle, etc. is made to contain in aliphatic polyester, the cast can be carried out to cooling drum lifting, an unextended sheet can be obtained, and many caves can be made to contain inside a film also by the method of subsequently to at least one or more axes extending.

[0016]In said polymer mixture, colorant, an illuminant-proof, a fluorescence agent, a spray for preventing static electricity, etc. may be added if needed.

[0017]The method of carrying out melting extrusion molding of said polymer mixture can apply the publicly known T-die method, a tubular film process, etc., and can obtain an unextended sheet by these methods. the range of melting temperature (T_m) - T_m+70 ** of the polymer which uses extrusion temperature -- it is the range of T_m+20-T_m+50 ** more preferably. It will extrude, if extrusion temperature is too low, and stability is difficult to get and falls into an overload easily. Since decomposition of polymer will become

intense if too conversely high, it is not desirable. The die of the extrusion machine used by this invention may have an annular or linear slit. The same grade as the extrusion temperature range may be sufficient as the temperature of a die.

[0018]In this way, it is preferred to extend the unextended sheet which consists of an obtained polymer mixture to at least 1 shaft orientations. As for the aliphatic polyester system film of this invention, it is still more preferred that it is the film by which heat setting was carried out after biaxial stretching, and it is extended [it produces it and] and manufactured by a publicly known method.

[0019]biaxial stretching of an unextended sheet may boil extension of eye one axis, and extension of eye two axes one by one, and may perform them, or may perform them simultaneously. Any may be sufficient as the extension (inflation extension) by extending by the extension (tenter extension) and pneumatic pressure by grasping and extending the method to the extension (roll extension) and the clip between rolls with the speed difference, etc. However, when it thinks from a mechanical property etc., the serial biaxial extension which is extended to the lengthwise direction which is equivalent to the flow direction of a film first, and then is extended in a transverse direction is preferred. Although concretely explained taking the case of this length and serial biaxial stretching extended in lateral order, if the below-mentioned film characteristic is satisfied, it will not be limited to the following methods.

[0020]Extension temperature has the preferred range of glass-transition-temperature (Tg) -Tg+50 ** of the polymer to be used. It is the range of Tg+10-Tg+40 ** still more preferably. Extension temperature is difficult to extend at below Tg, and if Tg+50 ** is exceeded, thickness uniformity and the obtained mechanical strength of a film fall, and it is not desirable.

[0021]Although at least one step of extension of length and width may be performed by dividing into a multi stage story, it is eventually preferred in each extension direction from the homogeneity of thickness, or a point of mechanical properties to extend 12 or more times still more preferably for 3.5 or more times, and length and plane-of-structure product magnification 9 or more-time still more preferably at least 3 or more times. It becomes difficult for length and a lateral orientation ratio to obtain 3 or less times, and for area magnification to obtain a thickness uniformity good film by 9 or less times, respectively, and sufficient improvement in physical properties, such as a mechanical strength, is hard to be obtained.

[0022]Vertical extension has preferred roll extension and the heating method of the sheet at the time of vertical extension may also be heating by a heating roller or infrared rays, or the other methods. A guide roll or a nip roll may be used for the arbitrary places of preheating and an extension roll. The tenter extension of lateral orientation is desirable.

[0023]In this invention, a film is heat-treated at 140-160 ** preferably [it is desirable and] to 130 ** - Tm, and a pan after the end of extension. At this time, a film with a smaller heat shrinkage rate is obtained by making it heat-treat, making length and/or a transverse direction ease not less than 2%. By adopting the above manufacturing conditions, the heat shrinkage rate of the longitudinal direction at 120 ** of the aliphatic polyester system biaxially oriented film in this invention can be made into 5% or less and 3 more% or less. Since wrinkles not only occur at the time of heat sealing, but it will become easy to generate a printing gap in presswork and solatium nature will be spoiled if a heat shrinkage rate is larger than 5%, it is not desirable.

[0024]In this invention, it is good also as what is called a complex film that laminated other layers at least on one side of the substrate film layer. How to laminate the thermoplastics fused at least on one side of the

aliphatic polyester system film which the method in particular is not limited and carried out biaxial extension, for example, The thermoplastics fused at least on one side of the film which carried out 1 axis extension is laminated, and it is not limited [method / the method of extending the layered product to rectangular directions further, / of pasting the already extended film together with adhesives or a binder / in particular]. However, when productivity is taken into consideration, after extruding the raw material of a surface and a central layer from a separate extrusion machine, leading it to one dice and obtaining an unextended sheet, the lamination what is called by a co-extrusion method which carries out orientation to at least 1 axis is the most preferred [a raw material].

[0025]In the case of a co-extrusion method, it becomes easy to obtain the film according to demand characteristics by containing what is respectively different by the surface and a central layer in additives, such as an inorganic particle, a spray for preventing static electricity, an ultraviolet ray absorbent, a fluorescent brightener, and an antioxidant. For example, in order to make a surface contain particles with larger particle diameter than a central layer in order to reconcile slide nature and concealment nature (opacity), and to reconcile an ultraviolet-rays preventive effect and concealment nature, Making a titanium dioxide, calcium carbonate, etc. contain etc. is mentioned to the rutile titanium dioxide which carried out ultraviolet inhibitor and a surface treatment, and a central layer at a surface.

[0026]Since adhesion of the ink used by offset printing or gravure printing or a toner is made more into fitness, a coating layer can be provided in a film surface. As a method of providing a coating layer, methods usually used, such as a gravure coating method, a kis coat method, a dip method, a spray coat method, a curtain coat method, an air knife coat method, a braid coat method, and a reverse roll coat method, are applicable. How to apply to the surface of the sheet for undivided [which consist of a polymer mixture before performing orientation treatment as a stage to apply] beforehand, Any methods, such as a method to which apply to the cavernous content film surface which carried out orientation to 1 shaft orientations, and rectangular directions are made to carry out orientation of it further, and the method of applying to the cavernous content film surface which orientation treatment ended, are possible.

[0027]In order to improve printing nature, corona treatment, plasma treatment, flame treatment, etc. may be performed on a film, and the surface energy of a film may be raised.

[0028]The white film or sheet obtained in this way, Since the adhesion of solatium nature, the ink which it tears, and a sex is good and is further used by offset printing or gravure printing, or a toner is good compared with the white film by which the conventional proposal is made, it is suitable as substrates, such as wrapping, printed matter, and information storage paper. In addition to this, a label, a poster, a card, a record paper, wrapping, inkjet printing paper, It can use for a video printer image receiving paper, a barcode label, a bar code printer image receiving paper, a thermographic recording paper, a map, dust-free paper, the plotting board, photographic paper, a tissue, wallpaper, a release paper, a calendar, a magnetic card, tracing paper, pressure sensitive paper, a copying paper, clinical laboratory test paper, etc.

[0029]

[Example]Although an example and a comparative example are given and the contents and the effect of this invention are explained concretely hereafter, this invention is not limited to the following examples, unless it deviates from the gist. The valuation method of the physical properties in the following examples and a comparative example is as follows.

[0030](1) Reduced viscosity (etas/C)

0.125 g of polymer was dissolved in 25 ml of chloroform, and it measured at 25 ** using the Ubbelohde viscosity pipe. A unit is dl/g.

[0031](2) Put a seal for a heat shrinkage rate film at intervals of 10 mm in width, 250-mm picking in length, and 200 mm, and measure the interval A by the fixed tension of 5 g. Then, it was no-load, the interval B of the seal after putting into the oven for 30 minutes and in 120 ** atmosphere was searched for, and the heat shrinkage rate of the direction of a film length hand was searched for by the following formulas.

Heat shrinkage rate (%) = $(A-B)/Ax100$ [0032](3) It carried out by solatium nature organoleptics, and when the sample of 15-mm-wide tape shape was cut by hand, what can be easily cut by hand from a film end was made into O, and what is not made was made into x.

[0033](4) According to total-light-transmittance JIS-K6714, the total light transmittance (%) of the film was measured using the POIKKU integrating sphere type H.T. R meter (product made from optics precision [Japanese]). It means that concealment nature is high, so that this value is small.

[0034](5) Start an apparent-specific-gravity film correctly in square of 10 cm x 10 cm, measure 50 points of the thickness, and ask for average thickness t (unit: micrometer). Next, the weight of a sample is measured to 0.1 mg and it is referred to as w (unit: g). And apparent specific gravity (g/cm^3) was calculated by the lower type.

Apparent-specific-gravity = $(w/t) \times 100$ [0035]To 80 % of the weight of Polly L-lactic acid of example 1 reduced-viscosity 2.10 dl/g, add 20 % of the weight of calcium carbonate with a mean particle diameter of 0.6 micrometer, and caliber the extrusion machine of 30 mm with a T die is used, After extruding with the resin temperature of 210 **, it cooled with a 20 ** chilled roll, and the 500-micrometer-thick unstretched film was obtained. After having preheated film temperature at 80 ** with two or more ceramics rolls, extending 3.5 times to the lengthwise direction with the stretching speed between rolls, extending 3.8 times at 80 ** with a tenter type drawing machine subsequently to a transverse direction and carrying out heat setting at 155 **, horizontal relaxation processing was performed 3% at 135 **. The 45-micrometer-thick oriented film was obtained. The physical properties are shown in Table 1.

[0036]In example 2 Example 1, 80 % of the weight of Polly L-lactic acid of reduced viscosity 2.10 dl/g is received, Polystyrene resin (Mitsui Chemicals G797N) was made into anatase type titanium dioxide (product made from Fuji titanium, TA-300) 5 weight section 15% of the weight, and the white Polly L-lactic acid film was obtained by the completely same method as claim 1 except the thickness of the last film having been 100 micrometers.

[0037]In example 3 Example 1, the white polylactic acid film was obtained by the completely same method as Example 1 instead of calcium carbonate except having used the condensation silica particle (the product made from Fuji SHIRISHIA, SAIRISHIA 310).

[0038]The white film was obtained by the completely same method as Example 2 except having used polyethylene terephthalate resin of limiting viscosity 0.62 instead of comparative example 1 polylactic resin. The obtained film was not able to be cut by a hand from an end.

[0039]the film obtained in four to example 6 Examples 1, 2, and 3 -- acrylic polyol resin (the product made from Dainippon Ink Chemicals.) BONKOTOHU596 and a cross linking agent (the product made from Dainippon Ink Chemicals, bar knock DN950) so that a weight ratio may be set to 100:20, It mixed to the mixed solvent of toluene/methyl ethyl ketone (=50/50; volume ratio), and the coat of the coating liquid

whose solids concentration is 20 % of the weight was carried out so that the amount of solid content might serve as 1 g/m². Desiccation was carried out for 1 minute at 120 **. The adhesive property with the spreading side of a coating film, the offset ink, UV ink, and gravure ink which were obtained was good.

[0040]

[Table 1]

	実施例1	実施例2	実施例3	比較例1
熱収縮率 (%)	2. 3	2. 4	2. 5	0. 2
手切れ性	○	○	○	×
光線透過率 (%)	24	8	19	8
見かけ比重 (g/cm ³)	1. 25	1. 05	1. 10	1. 07

[0041]

[Effect of the Invention] Since the aliphatic polyester system film of this invention has the printing clear nature which is the important characteristic in films for a package, such as a perishable food, a processed food, drugs, medical equipment, and electronic parts, and is further excellent in solatiom nature and twist stability, it is useful to the film for a package, adhesive tape, etc.

[Translation done.]